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Hetaryl Thioketones: Synthesis and Selected Reactions

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ABSTRACT: A series of phenyl/hetaryl and bishetaryl thioketones have been prepared via O/S exchange of the corresponding ketones by treatment with Lawesson's reagent. The non-symmetrical ketones were conveniently accessible via the reactions of lithiated furan and thiophene with N,N-dimethyl benzamide and hetarylcarboxamides, respectively, whereas the symmetrical ketones were obtained by treatment of ethyl N,N-dimethylcarbamate with two equivalents of lithiated heterocycles. Under typical conditions, selected examples of the hetaryl thioketones were oxidized selectively to give thiocarbonyl S-oxides (sulfines). Reactions with diazomethane at –65 °C yielded 1,3-dithiolanes in a regioselective manner and hetero-Diels-Alder reactions of 2-thienyl substituted thioketones with dimethyl acetylenedicarboxylate yielded the corresponding 7*H*-thieno[2,3-*c*]thiopyran-4,5-dicarboxylates.

KEYWORDS: thioketones, heterocumulenes, sulfines, thiocarbonyl ylides, 1,3-dipolar cycloadditions

INTRODUCTION

Dedicated to Prof. R. Okazaki on the occasion of his 77th birthday.

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It is well known that ketones form an important class of organic compounds with key importance for diverse applications in organic synthesis. The S-analogues, *i.e*. thioketones, are much less known as useful starting materials. Their availability and stability depend on the substitution pattern [1]. Whereas enolizable aliphatic thioketones are relatively unstable compounds [2], cycloaliphatic and aromatic thioketones, *e.g*. adamantanethione and thiobenzophenone, are isolable materials, which can be prepared from the corresponding ketones via O/S-exchange and stored under inert gas atmosphere for a longer time. Moreover, •heavy analogues of thioketones• bearing Si=S, Ge=S, etc. groups, stabilized by bulky substituents are also known as isolable compounds [3].

In the recent three decades, both cycloaliphatic and aromatic thioketones have extensively been studied as reactive substrates in 1,3-dipolar cycloadditions and hetero-Diels-Alder reactions [4]. Especially important is their high reactivity towards some types of 1,3-dipoles and dienes, which led to the creation of the terms •superdipolarophiles• and •superdienophiles' [5]. In addition, the oxidation of thioketones leading to thiocarbonyl S-oxides (sulfines) opens a convenient access to this class of reactive heterocumulenes [6]. Hetaryl thioketones are an attractive class of aromatic thioketones as the presence of an aromatic heterocycle influences their reactivity and physicochemical properties. For example, some aryl/hetaryl thioketones were found to be efficient inhibitors of some types of isomerases [7]. The aim of the present study was to elaborate a general method for the preparation of aryl/hetaryl and bishetaryl thioketones and to investigate their behavior in some typical reactions.

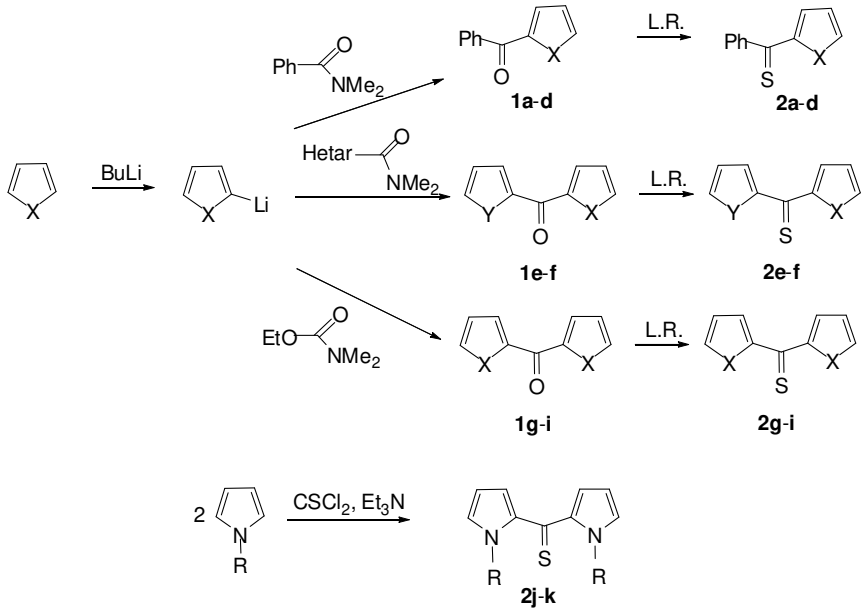
RESULTS AND DISCUSSION

Aromatic ketones can be conveniently converted into their sulfur analogues by treatment with Lawesson's reagent [8]. Therefore, the first part of the present study concerned an efficient and general method for the preparation of aryl/hetaryl and bishetaryl ketones **1**, which subsequently could be used for the synthesis of the corresponding thioketones **2**.

Various synthetic methods are known to prepare ketones of type **1**, but some of them, e.g. the acylation of furan or thiophene with benzoic acid, led to mixtures of products [9a]. A recently reported method, recommending Lewis acids such as $AlPW_{12}O_{40}$ [9b] or ZnO [9c], was inefficient in our laboratories. On the other hand, the best procedure for the preparation of non-symmetrical ketones **1** was based on the treatment of lithiated furan, thiophene, and

selenophene with the corresponding N,N-dimethylcarboxamides [10] (Scheme 1). In the case of symmetrical ketones **1**, two equivalents of the lithiated heterocycle were reacted with ethyl N,N-dimethylcarbamate.

The synthesis of bis-(pyrrol-2-yl) and bis-(*N*-methylpyrrol-2-yl) thioketones was performed via treatment of pyrrol or N-methylpyrrol with thiophosgene in the presence of triethylamine [11]. In all other cases, thioketones **2** were obtained in a typical manner from the corresponding ketones **1** and Lawesson's reagent in boiling toluene. All thioketones **2** were purified by column chromatography and isolated as colored oils or solids, which could be stored in dry ice without decomposition (Table 1). Thioketones **2d**, **f**, and **i**, containing a selenophene ring as substituent as well as the non-symmetrical thioketone **2e**, are new compounds.



SCHEME 1 Synthesis of aryl/hetaryl and bishetaryl thioketones

TABLE 1 Synthesis of aryl/hetaryl and bishetaryl thioketones

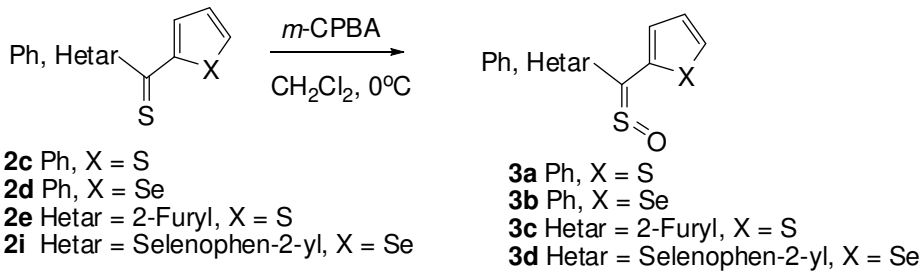
2	Ph/Hetar	X	Solvent/Temp.	React. time	Yield (%)[a)]
a [12]	Ph	MeN	Toluene/70 °C	6 h	94
b [13]	Ph	O	Benzene/80 °C	20 min	96
c [13]	Ph	S	Toluene/reflux	2 h	96
d	Ph	Se	Benzene/80 °C	1.5 h	81
e	2-Furyl	S	Toluene/reflux	1 h	80

f	2-Furyl	Se	Benzene/70 °C	0.5 h	74
g [14]	2-Furyl	O	Benzene/50 °C	2 h	90
h [14]	2-Thienyl	S	Toluene/55 °C	1.5 h	95
i	Selenophen-2-yl	Se	Benzene/70 °C	1 h	87
j [15]	Pyrrol-2-yl	NH	b)		70
k [15]	1-Methylpyrrol-2-yl	MeN	b)		68

[a]) Yield of isolated product after chromatography

[b]) Prepared via reaction with thiophosgene ($CSCl_2$)

Four of the prepared thioketones, **2c**-**e**, and **i** were treated with an equimolar amount of *meta*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 solution at 0 °C, and immediate decolorization was observed in all cases. The symmetrical bis(selenophen-2-yl)thioketone (**2i**) was converted to the corresponding sulfine **3d** and isolated as a crystalline material (92% yield; Scheme 2). In the $^{13}C\{^1H\}$ NMR spectrum, the characteristic absorption of the C=S=O group appeared at 178.9 ppm. In the case of the non-symmetrical **2e**, the respective sulfine **3c** was obtained as a mixture of *Z*- and *E*-isomer in a ratio of ca. 3:1 (configuration of major and minor isomer is unknown). Attempted separation of the isomers by preparative TLC was unsuccessful, and the presence of both isomers in the purified material was evidenced by two $^{13}C\{^1H\}$NMR signals at 169.5 and 170.1 ppm. However, the ratio of both isomers was changed to ca. 2:3. Unexpectedly, the mixture of almost equal amounts of *Z*- and *E*-sulfines **3a** obtained from thioketone **2c** gave, after separation on silica, only one sulfine in 90% yield. The same effect was also observed in the case of **3b** (obtained from **2d**). Apparently, in both cases one of the isomers underwent complete isomerization during the chromatographic workup.



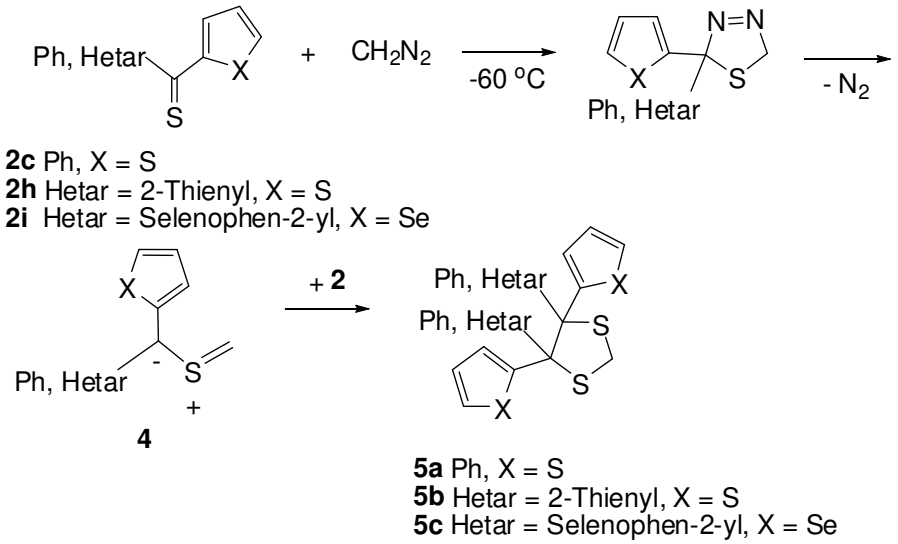
2c Ph, X = S
2d Ph, X = Se
2e Hetar = 2-Furyl, X = S
2i Hetar = Selenophen-2-yl, X = Se

3a Ph, X = S
3b Ph, X = Se
3c Hetar = 2-Furyl, X = S
3d Hetar = Selenophen-2-yl, X = Se

SCHEME 2 Oxidation of thioketones **2** to give sulfines **3**

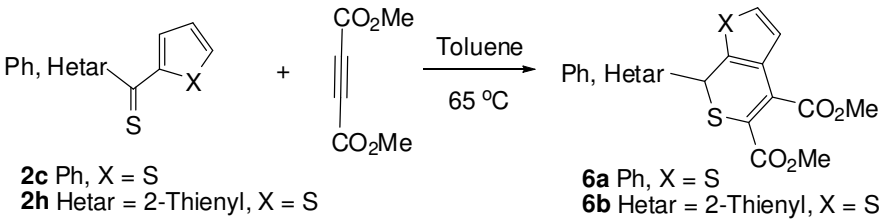
It is worth mentioning that in all cases the oxidation occurred selectively at the thiocarbonyl group and the heteroaromatic rings were not oxidized. The products **3** are relatively stable and did not decompose during the purification procedure.

It is well established that aromatic thioketones react easily with diazomethane, even at low temperature, and in the case of thiobenzophenone, the initially formed 1,3,4-thiadiazoline did not decompose at –60 °C [16]. The evolution of N_2 was observed only at –45 °C, and the intermediate thiocarbonyl ylide underwent either head-to-head dimerization or, in the presence of a suitable dipolarophile, was trapped forming the corresponding five–membered cycloadduct. Hetaryl thioketones **2c**, **h** and **i** also reacted smoothly with diazomethane at –60 °C, but, unexpectedly, a spontaneous elimination of N_2 was observed, and 1,3-dithiolanes **5a**–**c** were obtained as the exclusive products of a [2+3] cycloaddition of the intermediate thiocarbonyl ylides **4** with the starting thioketone **2** (Scheme 3). The non-symmetrical thioketone **2c** yielded a mixture of *Z*- and *E*-isomers of **5a** in a ratio of *ca*. 45:55. In all three cases, however, the formation of the 1,3-dithiolanes occurred regioselectively and 4,4,5,5-tetrasubstituted 1,3-dithiolanes were the products. The proof for this structure (and not 2,2,4,4-tetrasubstituted isomers) was the chemical shift of the CH_2 groups in the $^{13}C\{^1H\}$NMR spectra between 30.3 and 31.7 ppm, characteristic for its location between the two S-atoms [17]. The spontaneous elimination of N_2 at –60 °C is most likely the results of the influence of the hetaryl rings on the cycloreversion step leading to thiocarbonyl ylides **4**. Apparently, the subsequent [2+3] cycloaddition with the starting thioketone **2** is faster than the head-to-head dimerization or the 1,3-dipolar electrocyclization to give the corresponding thiiranes.



SCHEME 3 Reaction of thioketones **2** with diazomethane yielding 1,3-dithiolanes **5**

An interesting reaction displayed by some aromatic thioketones is the hetero-Diels-Alder reaction with acetylenic dienophiles [18] or benzyne [19]. To the best of our knowledge, hetaryl thioketones have not been studied in reactions with acetylenic dienophiles yet. However, their hetero-Diels-Alder reactions with electron-deficient ethylenes are known [20]. In our study, the experiments with dimethyl acetylenedicarboxylate were carried out with the non-symmetrical thioketone **2c** and the symmetrical **2h** in toluene in a closed glass tube at 65 °C. In both cases, the reaction was complete after 8 h. The product with **2h** was isolated in 72 % yield, and the spectroscopic data confirmed the expected structure **6b** (Scheme 4). For example, in the $^{13}C\{^{1}H\}$NMR spectrum, two C=O signals appeared at 164.3 ppm and 167.5 ppm, and the characteristic absorption of a sp^3-CH group was found at 39.1 ppm. The latter gave a singlet in the ^{1}H NMR spectrum located at 5.69 ppm. The analogous reaction with **2c** led regioselectively to a single product **6a**. The involvement of the hetaryl ring in the [4+2] cycloaddition was proved by the spectroscopic data. For example, two CH signals of the former 2-thienyl ring absorb as two doublets at 7.03 and 7.12 ppm with J = 5.4 Hz. Further signals in the ^{1}H-NMR spectrum evidenced the presence of an intact phenyl substituent.



2c Ph, X = S
2h Hetar = 2-Thienyl, X = S

6a Ph, X = S
6b Hetar = 2-Thienyl, X = S

SCHEME 4 Hetero-Diels-Alder reaction with hetaryl thioketones

These results correspond with the selectivity of the [4+2] cycloaddition observed with maleic anhydride and, for example **2c**, reported in [20a]. Also in these cases, only the hetaryl ring was involved in the hetero-Diels-Alder reaction. The formation of products **6** can be rationalized by a 1,3-H shift in the initially formed cycloadduct.

CONCLUSIONS

The described results show that a straightforward method for the preparation of symmetrical and non-symmetrical hetaryl thioketones comprises the reaction of lithiated five-membered

heterocycles with ethyl N,N-dimethylcarbamate and N,N-dimethylcarboxamides, respectively, followed by thionation with Lawesson's reagent. The procedure is of general importance and can be applied for N-substituted pyrrole, furan, thiophene, and selenophene derivatives. The obtained hetaryl thioketones are attractive building blocks for the preparation of S-containing heterocycles via 1,3-dipolar cycloadditions or hetero-Diels-Alder reactions. The oxidation of the hetaryl thioketones leads to new sulfines, which are versatile starting materials for the synthesis of more complex S-containing products.

EXPERIMENTAL

General

Melting points were determined in a capillary using a Melt-Temp. II (Aldrich) apparatus, and they are uncorrected. The IR spectra (KBr pellets or films) were recorded on a NEXUS FT-IR spectrophotometer; absorptions in cm^{-1}. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were measured on a Bruker Avance III (600 and 150 MHz, resp.) instrument, using solvent signals as reference. Chemical shifts (´) are given in ppm and coupling constants *J* in Hz. ESI-MS were recorded on a Varian 500 MS LC Ion Trap spectrometer. EI-MS and elemental analyses were performed in the Laboratory of the Polish Academy of Science (CBMiM) in Aódz.

Synthesis of non-symmetrical heteroaromatic ketones **1a–f**. Ketones **1a–f** were prepared according to the literature procedure by the treatment of lithiated furan, thiophene, and selenophene with the corresponding N,N-dimethylcarboxamides [10a].

(1-Methylpyrrol-2-yl)phenylmethanone (**1a**) [12]. Yield: 46%. Pale brown oil. ^{1}H NMR: 4.02 ($2CH_3N$); 6.14 (*dd*, $J_{H,H}$ = 4.0 Hz, $J_{H,H}$ = 2.5 Hz, $1CH_{arom}$); 6.72 (*dd*, $J_{H,H}$ = 4.0 Hz, $J_{H,H}$ = 1.7 Hz, $1CH_{arom}$); 6.89 (*br.t*, $J_{H,H}$ = 2.0 Hz, $1CH_{arom}$); 7.41–7.44 (*m*, $2CH_{arom}$); 7.49–7.52 (*m*, $1CH_{arom}$); 7.79–7.81 (*m*, $2CH_{arom}$).

2-Furyl(phenyl)methanone (**1b**) [13]. Yield: 45%. Yellow oil (solidified after cooling). ^{1}H NMR: 6.59 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.5 Hz, $1CH_{arom}$); 7.23 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 0.7 Hz, $1CH_{arom}$); 7.47–7.51 (*m*, $2CH_{arom}$); 7.57–7.60 (*m*, $1CH_{arom}$); 7.69–7.70 (*m*, $1CH_{arom}$); 7.96–7.98 (*m*, $2CH_{arom}$).

Phenyl(2-thienyl)methanone (**1c**) [13]. Yield: 76%. Mp = 46–48 °C. ^{1}H NMR: 7.16 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 3.4 Hz, 1CH$_{arom}$); 7.47–7.51 (*m*, 2CH$_{arom}$); 7.57–7.60 (*m*, 1CH$_{arom}$); 7.65 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.0Hz, 1CH$_{arom}$); 7.71 (*dd*, $J_{H,H}$ = 4.9 Hz, $J_{H,H}$ = 1.0Hz, 1CH$_{arom}$); 7.85–7.88 (*m*, 2CH$_{arom}$).

Phenyl(selenophen-2-yl)methanone (**1d**) [21]. Yield: 83%. Mp = 60–62 °C. ^{1}H NMR: 7.41–7.43 (1CH$_{arom}$); 7.48 (*br.t,* $J_{H,H}$ = 7.5 Hz, 2CH$_{arom}$); 7.58 (*br.t,* $J_{H,H}$ = 7.5 Hz, 1CH$_{arom}$); 7.83–7.86 (*m*, 3CH$_{arom}$); 8.43 (*dd*, $J_{H,H}$ = 5.5 Hz, $J_{H,H}$ = 0.7 Hz, 1CH$_{arom}$).

2-Furyl(2-thienyl)methanone (**1e**) [22]. Yield: 67%. Yellow oil (solidified after cooling). ^{1}H NMR: 6.58 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 1.3 Hz, 1CH$_{arom}$); 7.19 (*br.t*, $J_{H,H}$ = 4.1Hz, 1CH$_{arom}$); 7.38 (*d*, $J_{H,H}$ = 3.6 Hz, 1CH$_{arom}$); 7.66–7.69 (*m,* 2CH$_{arom}$); 8.15 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 0.6 Hz, 1CH$_{arom}$).

2-Furyl(selenophen-2-yl)methanone (**1f**). Yield: 82%. Mp = 48–50 °C (purified chromatographically (SiO_2) using a mixture of petroleum ether and ethyl acetate (8:2) as the eluent). ^{1}H NMR: 6.59 (*dd*, $J_{H,H}$ = 3.5 Hz, $J_{H,H}$ = 1.6 Hz, 1CH$_{arom}$); 7.38 (*dd*, $J_{H,H}$ = 3.5 Hz, $J_{H,H}$ = 0.4 Hz, 1CH$_{arom}$); 7.45 (*dd*, $J_{H,H}$ = 5.5 Hz, $J_{H,H}$ = 4.1 Hz, 1CH$_{arom}$); 7.65–7.67 (*m*, 1CH$_{arom}$); 8.41–8.44 (*m*, 2CH$_{arom}$). ^{13}C{^{1}H} NMR: 112.4, 118.7, 130.9, 136.1, 140.2, 146.2 (6CH$_{arom}$); 148.4, 152.2 (2C$_{arom}$); 174.4 (C=O). IR (KBr): 3114*m*, 3098*m*, 1606*s* (C=O), 1588*s*, 1564*s*, 1522*m*, 1465*vs*, 1420*vs*, 1306*vs*, 1237*m*, 1020*m*, 828*m*, 727*s*, 765*vs*. ESI-MS: 225 (46, [M(^{78}Se)]$^+$), 227 (100, [M(^{80}Se)]$^+$).

Synthesis of symmetrical heteroaromatic ketones **1g–i**. Ketones **1g–i** were prepared by the reaction of two equivalents of the corresponding lithiated heterocycle with ethyl N,N-dimethylcarbamate [10a,b].

Bis(2-furyl)methanone (**1g**) [14]. Yield: 56%. Mp = 31–33 °C. ^{1}H NMR: 6.54 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.7 Hz, 2CH$_{arom}$); 7.47 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 0.7 Hz, 2CH$_{arom}$); 7.62 (*dd*, $J_{H,H}$ = 1.7 Hz, $J_{H,H}$ = 0.7Hz, 2CH$_{arom}$).

Bis(2-thienyl)methanone (**1h**) [14]. Yield: 70%. Mp = 83–85 °C. ^{1}H NMR: 7.21 (*dd*, $J_{H,H}$ = 4.7 Hz, $J_{H,H}$ = 3.7 Hz, 2CH$_{arom}$); 7.72 (*d*, $J_{H,H}$ = 4.8 Hz, 2CH$_{arom}$); 7.93 (*d*, $J_{H,H}$ = 3.5 Hz, 2CH$_{arom}$).

Di(selenophen-2-yl)methanone (**1i**): Yield: 49%. Mp = 98–101 °C (purified chromatographically (SiO_2) using a mixture of petroleum ether and ethyl acetate (8:2) as the eluent). ^{1}H NMR: 7.44 (*dd*, $J_{H,H}$ = 5.5 Hz, $J_{H,H}$ = 3.9 Hz, $2CH_{arom}$); 8.08 (*dd*, $J_{H,H}$ = 3.9 Hz, $J_{H,H}$ = 1.0 Hz, $2CH_{arom}$); 8.41 (*dd*, $J_{H,H}$ = 5.5 Hz, $J_{H,H}$ = 1.00 Hz, $2CH_{arom}$). $^{13}C\{^1H\}$ NMR: 130.6, 135.2, 139.6 (3 signals for $6CH_{arom}$); 149.2 ($2C_{arom}$); 181.3 (C=O). IR (KBr): 3094*m*, 3081*m*, 1601*vs* (C=O), 1524*m*, 1517*m*, 1426*vs*, 1283*s*, 1082*s*, 735*s*, 710*vs*. ESI-MS: 287 (56), 289 (44, $M(^{78}Se)+1]^+$), 290 (17), 291 (100, $[M(^{80}Se)+1]^+$).

Synthesis of heteroaromatic thioketones **2a**–**i**. Thioketones **2a**–**i** were obtained in a typical manner from the corresponding ketones **1a**–**i** and Lawesson's reagent in boiling toluene or benzene [8].

(1-Methylpyrrol-2-yl)phenylmethanethione (**2a**) [12]. Yield: 94%. Violet oil. ^{1}H NMR: 6.20 (*dd*, $J_{H,H}$ = 4.2 Hz, $J_{H,H}$ = 2.6 Hz, $1CH_{arom}$); 6.62 (*dd*, $J_{H,H}$ = 4.2 Hz, $J_{H,H}$ = 1.7 Hz, $1CH_{arom}$); 7.13 (*br.t*, $J_{H,H}$ = 2.0 Hz, $1CH_{arom}$); 7.36–7.39 (*m*, $2CH_{arom}$); 7.46–7.49 (*m*, $1CH_{arom}$); 7.64–7.66 (*m*, $2CH_{arom}$).

2-Furyl(phenyl)methanethione (**2b**) [13]. Yield: 96%. Green oil. ^{1}H NMR: 6.60 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.7 Hz, $1CH_{arom}$); 7.11 (*d*, $J_{H,H}$ = 3.7 Hz, $1CH_{arom}$); 7.39 (*t*, $J_{H,H}$ = 7.6 Hz, $2CH_{arom}$); 7.50–7.53 (*m*, $1CH_{arom}$); 7.70–7.73(*m*, $2CH_{arom}$); 7.83–7.84 (*m*, $1CH_{arom}$).

Phenyl(2-thienyl)methanethione (**2c**) [13]. Yield: 96%. Dark–green oil. ^{1}H NMR: 7.15 (*dd*, $J_{H,H}$ = 5.1 Hz, $J_{H,H}$ = 4.0 Hz, $1CH_{arom}$); 7.38–7.42 (*m*, $3CH_{arom}$); 7.51–7.54 (*m*, $1CH_{arom}$); 7.68–7.70 (*m*, $2CH_{arom}$); 7.77 (*dd*, $J_{H,H}$ 5.1 Hz, $J_{H,H}$ = 1.1 Hz, $1CH_{arom}$).

Phenyl(selenophen-2-yl)methanethione (**2d**). Yield: 81%. Green crystals. Mp = 37–40 °C (hexane); purified chromatographically (SiO_2) using a mixture of pentane and CH_2Cl_2 (9:1) as the eluent. ^{1}H NMR: 7.38–7.41 (*m,* $2CH_{arom}$); 7.46 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 4.1 Hz, $1CH_{arom}$); 7.49–7.52 (*m*, $2CH_{arom}$); 7.67–7.68 (*m*, $2CH_{arom}$); 8.47 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 1.0 Hz, $1CH_{arom}$). $^{13}C\{^1H\}$ NMR: 127.9, 128.6, 130.9, 132.0, 133.4, 145.6 (6 signals for $8CH_{arom}$); 146.6, 162.6 ($2C_{arom}$); 225.4 (C=S). IR (KBr): 3073*w*, 1589*m*, 1505*s*, 1442*s*, 1406*vs*, 1336*vs*, 1240*vs*, 1173*m*, 1037*s*, 1046*m*, 863*m*, 712*vs,* 696*vs*. ESI-MS: 250 (15), 251 (44, $[M(^{78}Se)]^+$), 253 (100, $[M(^{80}Se)]^+$).

2-Furyl(2-thienyl)methanethione (**2e**). Yield: 80%. Dark–green oil (purified chromatographically (SiO_2) using a mixture of pentane and CH_2Cl_2 (6:4) as the eluent. ^1H NMR: 6.59 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.7 Hz, $1CH_{arom}$); 7.18 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 4.0 Hz, $1CH_{arom}$); 7.42 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 0.7 Hz, $1CH_{arom}$); 7.73 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 1.1 Hz, $1CH_{arom}$); 7.75 (*dd*, $J_{H,H}$ = 1.7 Hz, $J_{H,H}$ = 0.7 Hz, $1CH_{arom}$); 7.94 (*dd*, $J_{H,H}$ = 4.0 Hz, $J_{H,H}$ = 1.1 Hz, $1CH_{arom}$). $^{13}C\{^1H\}$ NMR: 113.7, 119.6, 128.8, 130.6, 136.8, 147.2 ($6CH_{arom}$); 151.9, 159.0 ($2C_{arom}$); 199.8 (C=S). IR (film): 3127*m*, 1603*m*, 1549*s*, 1508*s*, 1498*s*, 1450*vs*, 1407*vs*, 1387*s*, 1351*vs*, 1304*m*, 1254*s*, 1155*m*, 1039*s*, 1005*s*, 883*m*, 773*s,* 719*s*. ESI-MS: 193 (100, $[M–1]^+$), 194 (14, $[M]^+$), 196 (19).

2-Furyl(selenophen-2-yl)methanethione (**2f**). Yield: 74%. Green oil (purified chromatographically (SiO_2) using a mixture of pentane and CH_2Cl_2 (7:3) as the eluent. ^1H NMR: 6.58 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 1.7 Hz, $1CH_{arom}$); 7.41 (*d*, $J_{H,H}$ = 3.6 Hz, $1CH_{arom}$); 7.49 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 4.1 Hz, $1CH_{arom}$); 7.76 (*d*, $J_{H,H}$ = 1.4 Hz, $1CH_{arom}$); 8.16 (*dd*, $J_{H,H}$ = 4.1 Hz, $J_{H,H}$ = 0.9 Hz, $1CH_{arom}$); 8.45 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.9 Hz, $1CH_{arom}$). $^{13}C\{^1H\}$NMR: 113.8, 120.0, 132.0, 132.6, 144.2, 147.1 ($6CH_{arom}$); 158.3, 159.0 ($2C_{arom}$); 201.3 (C=S). IR (film): 3092*m*, 2924*m*, 1605*m*, 1547*s*, 1508*s*, 1448*s*, 1410*s*, 1334*s*, 1252*s*, 1153*m*, 1034*s*, 1002*s*, 883*m*, 735*s,* 703*s*. ESI-MS: 235 (100), 242 (34, $[M(^{80}Se)]^+$), 243 (12, $[M(^{80}Se)+1]^+$).

Bis(2-furyl)methanethione (**2g**) [14]. Yield: 90%. Green crystals. Mp = 51–52 °C. ^1H NMR: 6.61 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.7 Hz, $2CH_{arom}$); 7.53 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 0.7 Hz, $2CH_{arom}$); 7.77 (*dd*, $J_{H,H}$ = 1.7 Hz, $J_{H,H}$ = 0.7 Hz, $2CH_{arom}$).

Bis(2-thienyl)methanethione (**2h**) [14]. Yield: 95%. Green oil. ^1H NMR: 7.15 (*dd*, $J_{H,H}$ = 5.2 Hz, $J_{H,H}$ = 3.8 Hz, $2CH_{arom}$); 7.66 (*dd*, $J_{H,H}$ 3.8 Hz, $J_{H,H}$ = 1.1 Hz, $2CH_{arom}$); 7.73 (*dd*, $J_{H,H}$ = 5.2 Hz, $J_{H,H}$ = 1.1 Hz, $2CH_{arom}$).

Di(selenophen-2-yl)methanethione (**2i**). Yield: 87%. Green crystals. Mp = 95–97 °C (hexane); purified chromatographically (SiO_2) using a mixture of pentane and CH_2Cl_2 (7:3) as the eluent. ^1H NMR: 7.46 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 4.0 Hz, $2CH_{arom}$); 7.80 (*dd*, $J_{H,H}$ = 4.0 Hz, $J_{H,H}$ = 1.0 Hz, $2CH_{arom}$); 8.42 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 1.0 Hz, $2CH_{arom}$). $^{13}C\{^1H\}$NMR: 131.3, 131.7, 142.9 ($6CH_{arom}$); 159.6 ($2C_{arom}$); 212.4 (C=S). IR (KBr): 3090*m*, 1655*m*, 1509*s*,

1508*s*, 1410*vs*, 1337*s*, 1325*s*, 1304*m*, 1271*s*, 1240*vs*, 1152*s*, 1075*m*, 1037*vs*, 1005*s*, 852*s*, 708*vs,* 690*s*. ESI-MS: 303 (62), 305 (92, $[M(^{78}Se)+1]^+$), 307 (100, $[M(^{80}Se)+1]^+$).

Synthesis of heteroaromatic thioketones **2j**–**k**. The bis(pyrrol-2-yl) and bis(*N*-methylpyrrol-2-yl)thioketones **2j** and **2k** were prepared by treatment of pyrrol or N-methylpyrrol with thiophosgene in the presence of triethylamine according to the literature procedure [11].

*Bis(1*H*-pyrrol-2-yl)methanethione* (**2j**) [15]. Yield: 70%. Violet crystals. Mp = 96–98 °C. ^{1}H NMR: 6.43–6.45 (*m*, $2CH_{arom}$); 7.07–7.08 (*m*, $2CH_{arom}$); 7.23–7.24 (*m*, $2CH_{arom}$); 9.80 (*br.s*, 2NH).

Bis(1-methylpyrrol-2-yl)methanethione (**2k**) [15]. Yield: 68%. Violet crystals. Mp = 100–101 °C. ^{1}H NMR: 3.94 (*s*, $2N–CH_3$); 6.12 (*dd*, $J_{H,H}$ = 3.9 Hz, $J_{H,H}$ = 2.6 Hz, $2CH_{arom}$); 6.55 (*dd*, $J_{H,H}$ = 3.9 Hz, $J_{H,H}$ = 1.8 Hz, $2CH_{arom}$); 6,95 (*br.t*, $J_{H,H}$ = 1.9 Hz, $2CH_{arom}$).

Oxidation of thioketones **2c**-**e**, *and* **i**. 1 Mmol of the corresponding thioketone was treated with an equimolar amount of *meta*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 solution at 0 °C according to the known procedure [23]. The products were isolated on preparative plates coated with silica gel using a the mixture of petroleum ether and dichloromethane (3:2) as the eluent.

2-[Phenyl(sulfinyl)methyl]thiophene (**3a**). Yield: 190 mg (86%). Yellow oil. ^{1}H NMR (major isomer, after purification on SiO_2): 7.19 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 4.2 Hz, $1CH_{arom}$); 7.49–7.57 (*m*, $6CH_{arom}$); 7.75 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 0.9 Hz, $1CH_{arom}$). $^{13}C\{^1H\}$NMR (after purification on SiO_2): 126.5, 128.9, 129.7, 130.8, 131.0, 132.5 (6 signals for $8CH_{arom}$); 130.1, 138.0 ($2C_{arom}$); 181.4 (C=S=O). IR (film; after purification on SiO_2): 3078*m*, 3031*m*, 1675*m*, 1634*m*, 1573*m*, 1485*s*, 1443*vs*, 1406*vs*, 1363*s*, 1303*m*, 1244*s*, 1212*m*, 1159*m*, 1096*vs*, 1074*s*, 1056*s*, 1032*s*, 1004*s*, 962*s*, 840*vs*, 756*s*, 698*s*, 603*s*. ESI-MS (after purification on SiO_2): 221 (12, $[M+1]^+$), 243 (100, $[M+Na]^+$), 244 (13).

2-[Phenyl(sulfinyl)methyl]selenophene (**3b**). Yield: 206 mg (77%). Yellow oil. ^{1}H NMR (characteristic signals taken from the spectrum of the crude mixture): 7.41 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 4.3 Hz, $1CH_{arom}$) and 8.63 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.6 Hz, $1CH_{arom}$) (major isomer); 7.35 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 4.3 Hz, $1CH_{arom}$) and 8.28 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.6 Hz,

1CH_{arom}) (minor isomer). ^{1}H NMR (after purification on SiO_2): 7.41 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 4.3 Hz, 1CH_{arom}); 7.46–7.57 (*m*, 6CH_{arom}); 8.63 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.6 Hz, 1CH_{arom}). $^{13}C\{^{1}H\}$ NMR (after purification on SiO_2): 128.1, 128.9, 129.7, 130.7, 132.7, 139.6 (6 signals for 8CH_{arom}); 130.0, 140.1 (2C_{arom}); 183.7 (C=S=O). IR (film, after purification on SiO_2): 3058*m*, 3031*m*, 1626*w*, 1634*m*, 1501*m*, 1490*s*, 1443*s*, 1409*s*, 1350*s*, 1303*m*, 1241*s*, 1177*m*, 1092*s*, 1066*s*, 1051*s*, 1030*s*, 1001*s*, 918*m*, 849*m*, 752*s*, 696*s*, 625*s*. ESI-MS: 267 (56, [M(^{78}Se)]$^+$), 269 (100, [M(^{80}Se)]$^+$);

2-[Sulfinyl(2-thienyl)methyl]furan (**3c**) (mixture of two isomers). Yield: 122 mg (58%). Yellow oil. ^{1}H NMR (mixture of two isomers): 6.57 (*dd*, $J_{H,H}$ = 3.4 Hz, $J_{H,H}$ = 1.8 Hz, 1CH_{arom}); 6.73 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 1.7 Hz, 1CH_{arom}); 6.88 (*d*, $J_{H,H}$ = 3.4 Hz, 1CH_{arom}); 7.17 (*dd*, $J_{H,H}$ = 5.0 Hz, $J_{H,H}$ = 3.6 Hz, 1CH_{arom}); 7.23 (*dd*, $J_{H,H}$ = 4.9 Hz, $J_{H,H}$ = 4.1 Hz, 1CH_{arom}); 7.47 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 1.0 Hz, 1CH_{arom}); 7.62 (*dd*, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 1.0 Hz, 1CH_{arom}); 7.65 (*d*, $J_{H,H}$ = 1.4 Hz, 1CH_{arom}); 7.75–7.76 (*m*, 2CH_{arom}); 7.72 (*dd*, $J_{H,H}$ = 4.1 Hz, $J_{H,H}$ = 1.0 Hz, 1CH_{arom}); 8.27 (*d*, $J_{H,H}$ = 3.6 Hz, 1CH_{arom}). $^{13}C\{^{1}H\}$ NMR (mixture of two isomers): 112.1, 113.3, 113.8, 120.9, 126.8, 128.0, 128.7, 130.6, 131.0, 132.2, 144.1, 146.9 (12CH_{arom}); 128.5, 135.1, 143.9, 147.6 (4C_{arom}); 169.5, 170.1 (2C=S=O). IR (film): 3135*m*, 3104*m*, 2981*m*, 1622*m*, 1545*s*, 1496*s*, 1408*vs*, 1386*s*, 1304*m*, 1218*s*, 1196*m*, 1096*vs*, 1076*s*, 1056*s*, 1024*s*, 991*s*, 969*s*, 833*vs*, 749*vs*, 714*vs*, 667*s*. ESI-MS: 211 (100, [M+1]$^+$), 212 (14).

2-[Selenophen-2-yl(sulfinyl)methyl]selenophene (**3d**). Yield: 296 mg (92%). Yellow crystals. Mp = 82–84 °C (hexane/CH_2Cl_2). ^{1}H NMR: 7.42 (*dd*, $J_{H,H}$ = 5.7 Hz, $J_{H,H}$ = 3.8 Hz, 1CH_{arom}); 7.45 (*dd*, $J_{H,H}$ = 5.7 Hz, $J_{H,H}$ = 4.3 Hz, 1CH_{arom}); 7.55 (*dd*, $J_{H,H}$ = 3.8Hz, $J_{H,H}$ = 1.1 Hz, 1CH_{arom}); 8.00 (*dd*, $J_{H,H}$ = 4.3 Hz, $J_{H,H}$ = 1.1 Hz, 1CH_{arom}); 8.33 (*dd*, $J_{H,H}$ = 5.7 Hz, $J_{H,H}$ = 1.1 Hz, 1CH_{arom}); 8.62 (*dd*, $J_{H,H}$ = 5.7 Hz, $J_{H,H}$ = 1.2 Hz, 1CH_{arom}). $^{13}C\{^{1}H\}$ NMR: 128.3, 130.2, 131.2, 132.9, 136.5, 139.8 (6CH_{arom}); 159.6 (2C_{arom}); 178.9 (C=S=O). IR (KBr): 3094*m*, 3049*m*, 1604*m*, 1529*m*, 1508*s*, 1444*m*, 1404*vs*, 1351*s*, 1325*m*, 1280*m*, 1238*m*, 1162*m*, 1084*s*, 1057*vs*, 1042*vs*, 1033*vs*, 1005*s*, 950*s*, 845*m*, 728*vs,* 692*s*. ESI-MS: 321 (14, [M+1]$^+$), 343 (100, [M+Na]$^+$), 359 (23, [M+K]$^+$).

Reaction of thioketones **2c**, **h**, *and* **i** *with diazomethane*. 1 Mmol of the corresponding thioketone was treated with an excess of diazomethane solution in diethyl ether at –60 °C according to a known procedure [16]. Decolorization of the reaction mixtures was observed at

–60 °C. For thioketones **2c**, **h**, spontaneous elimination of nitrogen was observed at –60 °C. Pure products were isolated after chromatography on silica gel or by crystallization.

4,5-Diphenyl-4,5-bis(thienyl)-1,3-dithiolane (**5a**) (as the mixture of (*Z*)- and (*E*)-isomers). Yield: 305 mg (72%). Pale yellow crystals (hexane/CH_2Cl_2). Mp = 176 °C (dec.; purified chromatographically (SiO_2) using a mixture of petroleum ether and dichloromethane (3:2) as the eluent). ^{1}H NMR (mixture of isomers): 3.84, 3.94 (*AB*-system for (*Z*)-isomer, $J_{H,H}$ = 9.4 Hz, CH_2S); 3.99 (*s* for (*E*)-isomer, CH_2S); 6.70 (*dd*, $J_{H,H}$ = 3.8 Hz, $J_{H,H}$ = 1.1 Hz, $1CH_{arom}$); 6,76 (*dd*, $J_{H,H}$ = 5.1 Hz, $J_{H,H}$ = 3.8 Hz, $2CH_{arom}$); 6.80 (*dd*, $J_{H,H}$ = 5.1 Hz, $J_{H,H}$ = 3.8 Hz, $2CH_{arom}$); 6.94 (*dd*, $J_{H,H}$ = 6.7 Hz, $J_{H,H}$ = 1.2 Hz, $2CH_{arom}$); 7.07–7.11 (*m*, $4CH_{arom}$); 7.14–7.20 (*m*, $11CH_{arom}$); 7.22–7.24 (*m*, $3CH_{arom}$); 7.32–7.34 (*m*, $3CH_{arom}$); 7.43–7.45 (*m*, $4CH_{arom}$). $^{13}C\{^1H\}$ NMR (mixture of isomers): 30.3, 30.9 ($2CH_2$); 75.3, 75.5 ($4C_q$); 125.3, 125.4, 125.9, 126.2, 126.5, 127.2, 127.7, 130.0, 130.1, 130.4, 130.9 (11 signals for $16CH_{arom}$); 141.4, 141.9, 148.1, 149.6 ($8C_{arom}$). IR (KBr) (mixture of isomers): 3098*m*, 3058*m*, 1596*m*, 1580*m*, 1488*s*, 1441*s*, 1231*vs*, 1158*m*, 1118*m*, 1033*m*, 970*m*, 908*m*, 707*vs*. EI-MS: 422 (5, $[M]^+$), 171 (100).

4,4,5,5-Tetra(2-thienyl)-1,3-dithiolane (**5b**). Yield: 315 mg (73%). Pale pink crystals (petroleum ether/CH_2Cl_2). Mp = 179 °C (dec.). ^{1}H NMR: 4.18 (*s*, CH_2); 6.86–6.89 (*m*, $9CH_{arom}$); 7.24 (*dd*, $J_{H,H}$ = 4.9 Hz, $J_{H,H}$ = 1.4 Hz, $3CH_{arom}$). $^{13}C\{^1H\}$ NMR: 31.7 (CH_2); 73.1 ($2C_q$); 125.9, 126.6, 129.7 ($12CH_{arom}$); 145.9 ($4C_{arom}$). IR (KBr): 3094*m*, 3071*m*, 1630*m*, 1421*m*, 1441*s*, 1347*m*, 1230*s*, 1130*m*, 1113*m*, 1073*m*, 1044*m*, 852*m*, 837*m*, 705*vs*. EI-MS: 434 (5, $[M]^+$), 210 (100).

4,4,5,5-Tetra(selenophen-2-yl)-1,3-dithiolane (**5c**) (unstable, quickly decomposed during the purification). Yield: 405 mg (65%). Brown-yellow crystals (hexane/CH_2Cl_2). Mp = 170 °C (dec.). ^{1}H NMR: 4.13 (*s*, CH_2); 7.12 (*dd*, $J_{H,H}$ = 5.8 Hz, $J_{H,H}$ = 4.0 Hz, $4CH_{arom}$); 7.21 (*dd*, $J_{H,H}$ = 4.0 Hz, $J_{H,H}$ = 1.0 Hz, $4CH_{arom}$); 7.98 (*dd*, $J_{H,H}$ = 5.8 Hz, $J_{H,H}$ = 1.0 Hz, $4CH_{arom}$). $^{13}C\{^1H\}$ NMR: 30.9 (CH_2); 60.0 ($2C_q$); 128.2, 132.6, 133.8 ($12CH_{arom}$); 152.5 ($4C_{arom}$). IR (KBr): 3087*m*, 3053*m*, 1631*m*, 1437*m*, 1412*m*, 1328*m*, 1230*s*, 1128*m*, 1101*m*, 1056*m*, 1022*m*, 846*m*, 733*m*, 687*vs*.

Reaction of thioketones **2c**, **h** *with dimethyl acetylenedicarboxylate*. A solution of 1 mmol of the corresponding thioketone and 2 mmol of dimethyl acetylenedicarboxylate in 1 mL of dry

toluene [18] was placed in a closed glass tube. The mixture was heated at 65 °C for 8 h. The solvent was evaporated in vacuo. Subsequent separation on preparative plates coated with silica gel (eluent: CH_2Cl_2) gave pure products.

*Dimethyl 7-(2-thienyl)-7*H-*thieno[2,3-*c*]thiopyran-4,5-dicarboxylate* (**6a**). Yield: 253 mg (72%). Yellow crystals. Mp = 94.2–94.6 °C. ^{1}H NMR: 3.72, 3.84 (2*s*, $2CH_3O$); 5.69 (*s*, CH); 6.85 (*s*, 2 CH_{arom}); 7.02–7.03 (*m*, 1 CH_{arom}) 7.14–7.15 (*m*, 1 CH_{arom}); 7.18–7.19 (*m*, 1 CH_{arom}). $^{13}C\{^1H\}$NMR: 39.0 (CH); 52.9, 52.9 ($2CH_3O$); 123.3 ($1C_{arom}$); 124.5, 125.9, 126.4, 126.4, 127.0 ($5CH_{arom}$); 131.8, 132.6, 135.2, 142.9 ($4C_{arom}$); 164.3, 167.5 (2C=O). IR (KBr): 3093*w*, 2942*w*, 1733*s*, 1724*s*, 1572*w*, 1520*w*, 1432*m*, 1250*s*,1234*s*, 1095*w*, 728*m*. EI-MS: 293 (73, $[M–CO_2Me]^+$), 351 (47), 352 (100, $[M]^+$), 353 (24, $[M+1]^+$). Anal. Calc. for $C_{15}H_{12}S_3O_4$ (352.45): C 51.14, H 3.41, S 27.27; found: C 50.92, H 3.47, S 27.09.

*Dimethyl 7-phenyl-7*H-*thieno[2,3-*c*]thiopyran-4,5-dicarboxylate* (**6b**). Yield: 197 mg (57%). Yellow crystals. Mp = 85.9–86.3 °C. ^{1}H NMR: 3.70, 3.84 (2*s*, $2CH_3O$); 5.45 (*s*, CH); 7.03 (*d*, $J_{H,H}$ = 5.4 Hz, 1 CH_{arom}); 7.12 (*d*, $J_{H,H}$ = 5.4 Hz, 1 CH_{arom}) 7.25–7.27 (*m*, 5 CH_{arom}). $^{13}C\{^1H\}$ NMR: 43.9 (CH); 52.8, 52.9 ($2CH_3O$); 124.1 ($1C_{arom}$); 124.7, 125.9, 128.0, 128.7, 129.0,129.0, 129.5 ($7CH_{arom}$); 131.7, 133.1, 135.4, 139.4 ($4C_{arom}$); 164.3, 167.6 (2C=O). IR (KBr): 2944*w*, 1736*s*, 1725*s*, 1571*w*, 1434*m*, 1246*s*, 1221*s*, 1094*m*, 706*m*. EI-MS: 269 (100, $[M–C_6H_5]^+$), 346 (48, $[M]^+$), 347 (11, $[M+1]^+$). Anal. Calc. for $C_{17}H_{14}S_2O_4$ (346.43): C 58.96, H 4.05, S 18.50; found: C 58.92, H 4.11, S 18.56.

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